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The Co-Mn-Mo (Cobalt-Manganese-Molybdenum) System

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Introduction

The Co-Mn-Mo system was studied with the intent of establishing whether the complex intermediate σ and μ phases existing in the binary systems can be classified as electron compounds or size compounds. Two isothermal sections were established for this purpose and are reported here.

Binary Systems

The Co-Mn system [Massalski 2] (Fig. 1) shows a peritectic reaction L + (δ Mn) ↔ (β Mn) at ~1185 °C and a eutectic reaction L ↔ (γ Co) + (β Mn) at 1161 °C, where (γ Co) is the face-centered-cubic (fcc) terminal solid solution of Co. The (γ Mn) phase forms through a peritectoid reaction (δ Mn) + (β Mn) ↔ (γ Mn) at ~1154 °C. A wide β Mn phase field exists from Mn to the middle of the phase diagram. At ≤ 727 °C the β Mn → α Mn transformation occurs at the Mn side of the Co-Mn diagram. One intermediate phase CoMn forms through a peritectoid reaction (β Mn) + (γ Co) ↔ CoMn at ~545 °C. At the Co end of the Co-Mn system (γ Co) → (ε Co) phase transformation occurs at ≤ 422 °C where (ε Co) is the hcp terminal solid solution of Co.

The Co-Mo system [Massalski 2] (Fig. 2) has four intermediate phases Co_9Mo_2, Co_3Mo, Co_7Mo_6 (μ) and σ of which the latter two phases form through peritectic reactions L + (Mo) ↔ σ at 1620 °C and $L + \sigma \leftrightarrow \mu$ at 1510 °C A eutectic reaction $L \leftrightarrow \mu$ + (γ Co) occurs at 1335 °C. Three peritectoid reactions μ + (γ Co) ↔ Co_9Mo_2, Co_9Mo_2 + μ ↔ Co_3Mo and possibly (γ Co) + Co_3Mo ↔ (ε Co) occur at 1200, 1025, and ~700 °C, respectively. The Co_9Mo_2 and σ phases undergo eutectoid decomposition Co_9Mo_2 ↔ (γ Co) + Co_3Mo at 1018 °C and σ ↔ (Mo) + μ at 1000 ± 100 °C.

The Mn-Mo system, which was calculated on the basis of a thermodynamic model [Massalski 2] (Fig. 3), shows equilibrium of (α Mn) with Mn (gas) above 2220 °C and below this temperature liquid Mn exists. Two intermediate phases, Mn_5Mo_4 and σ, exist in the Mn-Mo system and both of them form through peritectic reaction (Mo) + $L \leftrightarrow Mn_5Mo_4$ at ~1500 °C and Mn_5Mo_4 + L ↔ σ at ~1400 °C, the latter phase transforms eutectoidally σ ↔ Mn_5Mo_4 + (α Mn) at ~1090 °C. At the Mn end the (δ Mn) phase forms through a peritectic reaction $L + \sigma \leftrightarrow$ δ Mn at ~1300 °C and decomposes through a eutectoid reaction (δ Mn) ↔ (β Mn) + (γ Mn) at ~1100 °C. The (β Mn) phase forms through a peritectoid reaction σ + (δ Mn) ↔ (β Mn) at ~1100 °C.

Binary and Ternary Phases

In the three binary systems Co-Mn, Co-Mo, and Mn-Mo six intermediate phases form. In the Co-Mn-Mo system two ternary intermediate phases, R and P, form. The structure data for all the binary and ternary phases are given in Table 1.

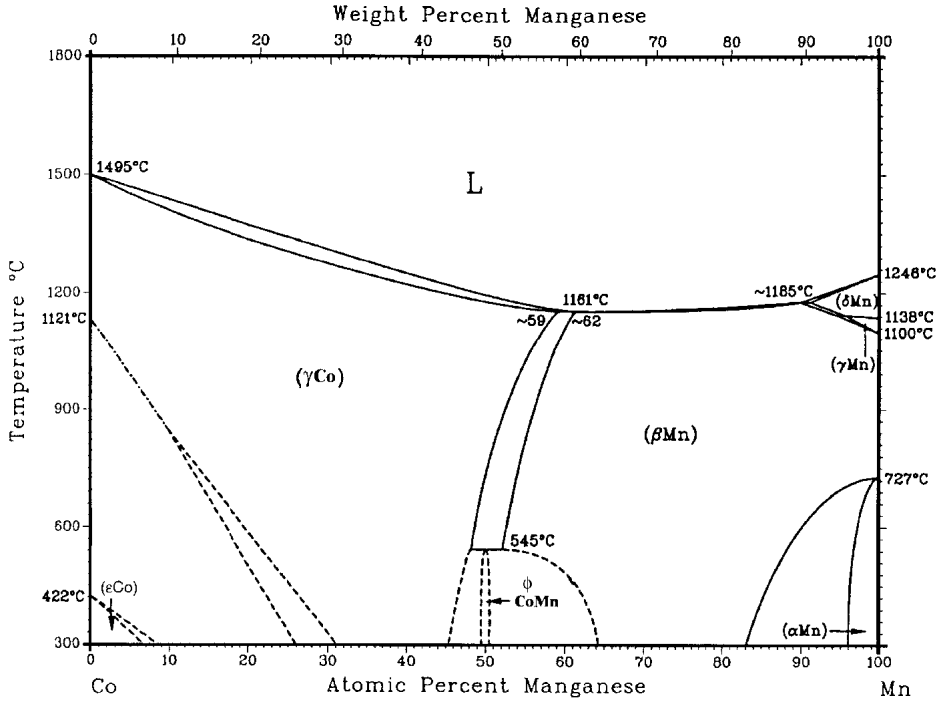

Fig. 1 Co-Mn binary phase diagram

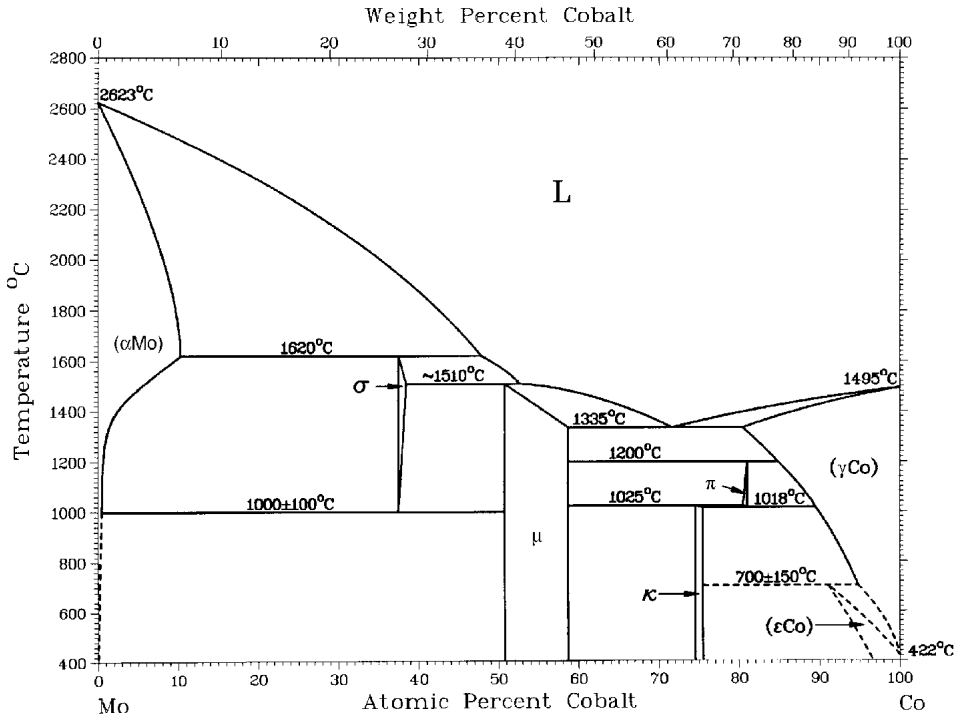

Fig. 2 Co-Mo binary phase diagram

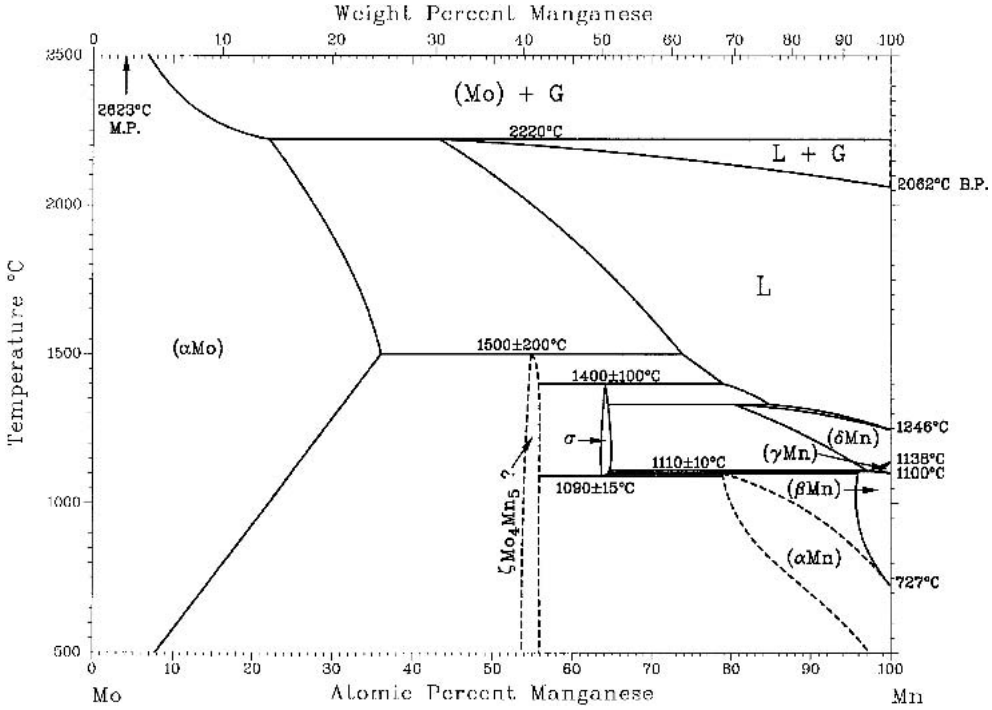

Fig. 3 Mn-Mo binary phase diagram

Ternary System

The Co-Mn-Mo system has been studied by [1960 Das]. The alloys up to ~ 50 at % Mo were prepared by induction melting in recrystallized alumina crucibles under argon atmosphere. Electrolytic Co, electrolytic Mn and Mo rod, all of high purity, were used to prepare the alloys. Preparation of alloys above ~50 at .% Mo was not extensively pursued due to excessive Mn loss and to development of segregation in the alloys. A few binary σ phase alloys were prepared for the Mn-Mo system by employing powder metallurgy methods. The alloys were homogenized at 1175° and 1240 °C for

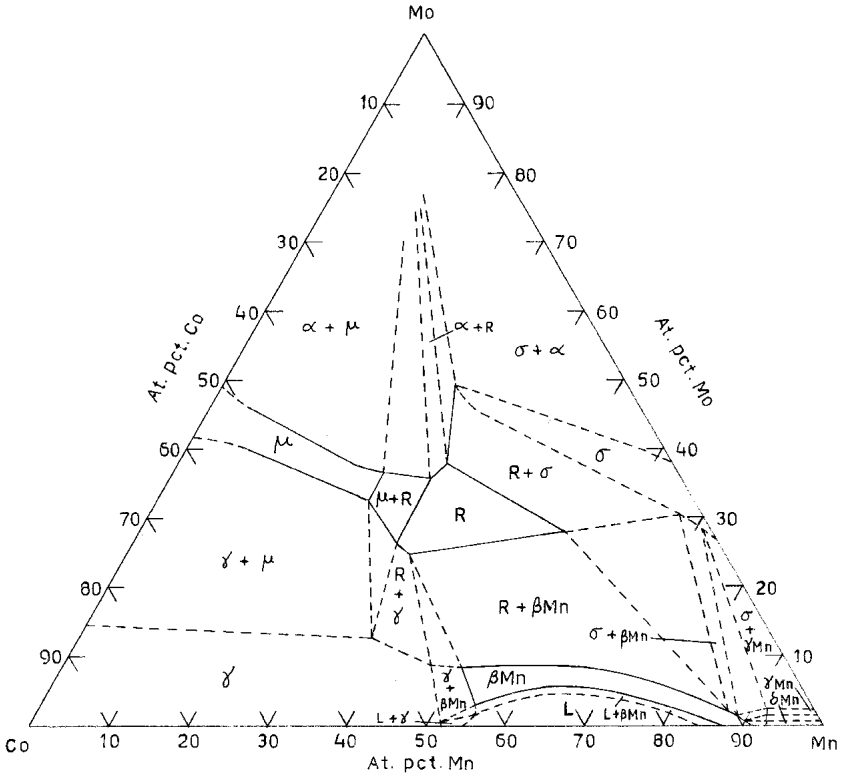

Fig. 4 1175 °C isothermal section of Co-Mn-Mo system. [1960 Das]

Table 1 Phases of the Co-Mn, Co-Mo, Mn-Mo Binaries and Co-Mn-Mo Ternary Systems

Phase Designation	Composition	Pearson's Symbol	Space Group	Type	Lattice Parameters, nm	
					a	*c*
α	(αMo)	*cI*2	$Im\bar{3}m$	W	…	…
γ	(γCo)	*cF*4	$Fm\bar{3}m$	Cu	…	…
ϵ	(ϵCo)	*hP*2	$P6_3/mcm$	Mg	…	…
αMn	(αMn)	*cI*58	$I\bar{4}3m$	αMn	…	…
βMn	(βMn)	*cP*20	$p4_132$	βMn	…	…
γMn	(γMn)	*cF*4	$Fm\bar{3}m$	Cu	…	…
δMn	(δMn)	*cI*2	$Im\bar{3}m$	W	…	…
ϕ	CoMn	…	…	(a)	…	…
π	Co_9Mo_2	*h*	…	…	0.25973	0.42123
κ	Co_3Mo	*hP*8	$P6_3/mcm$	Ni_3Sn	0.51245	0.41125
μ	Co_7Mo_6	*hR*13	$R\bar{3}m$	Fe_7W_6	0.4762	2.5015 (b)
σ	Co_9Mo_{15}	*tP*30	$P4_2/mnm$	σ(CrFe)	0.92287	0.48269
	Mn_2Mo	…	…	…	0.91	0.474
ξ	Mn_5Mo_4	*hR*39	…	…	…	…
R	$Co_{32}Mn_{36.5}Mo_{31.5}$	*hR*53	$R\bar{3}$	*R*(Mo,Cr,Co)	1.099	1.947 (b)
P	$Co_{29}Mn_{26}Mo_{45}$	*oP*56	*Pbnm*	*P*(Mo,Cr,Ni)	(c)	…

(a) Reported to be σ type
(b) Lattice parameters are for hexagonal cell.
(c) Lattice parameter not reported in [1960 Das]

72 h in evacuated and sealed fused silica tubes. Alloys relevant to the phase boundaries were chemically analyzed to determine their compositions. Metallography and x-ray diffraction methods were used for phase identification and phase boundary determination.

The 1175 °C isothermal section established by [1960 Das] is given in Fig. 4. In this study the redetermined binary σ phase boundaries of the Mn-Mo system at 1175 °C were found to be at ~27 at .% and ~38 at .% Mo. The σ phase region was found to extend from the Mn-Mo binary (up to ~20 at .% Co) toward the Co-Mo binary in which a σ phase also exists above 1000° ± 100 °C. Since a σ phase is known

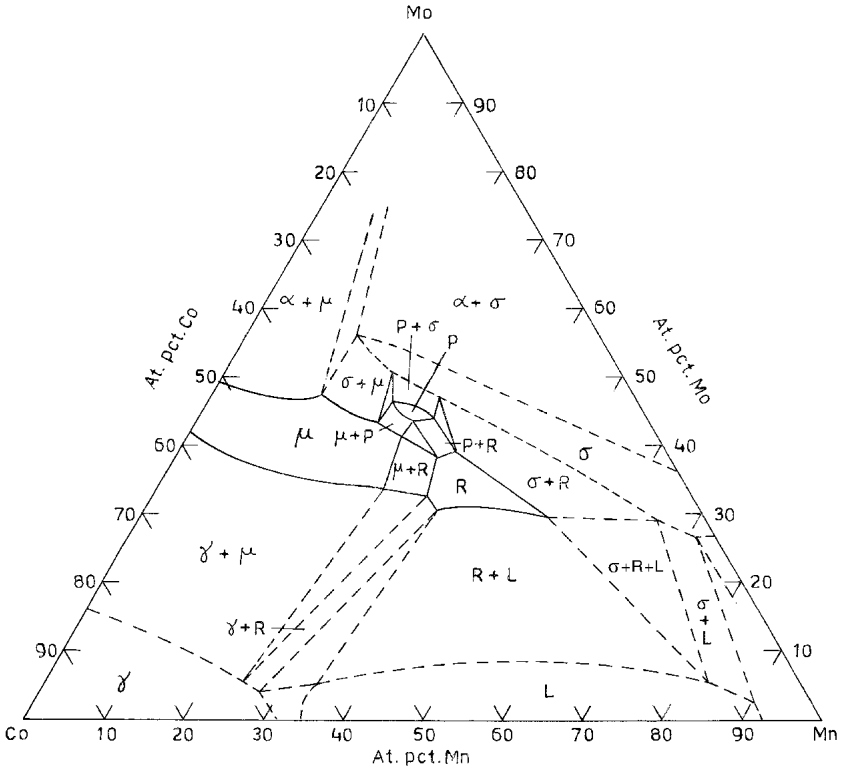

Fig. 5 1240 °C isothermal section of Co-Mn-Mo system. [1960 Das]

to exist in the Co-Mo binary it is surprising that the σ phase region does not extend from the Mn-Mo to the Co-Mo binary at 1175 °C. The μ phase existing in the Co-Mo system has been found to extend into the ternary system up to ~27 at .% Mn. Along the same direction of extension of the μ phase a ternary R phase occurs between ~33 at .% to ~54 at .% Mn. The direction of extension of the μ and R phases are approximately parallel to the extension of the σ phase region. At 1175 °C the β Mn phase extended as a narrow phase region almost parallel to the extensions of the σ, μ, and R phases. On the basis of the almost parallel extensions of the σ, μ, R, and β-Mn phases it was concluded that all these phases could possibly be classified as electron compounds of the σ phase type. The phase boundaries of the γ, γ Mn, δ Mn, and L regions were not determined and approximate locations of the phase boundaries are shown in Fig. 4.

The 1240 °C isothermal section was established with only a few alloys to find the extensions of the phases into the Co-Mn-Mo ternary (Fig. 5). As in the 1175 °C, the σ phase extended in the same direction but up to ~30 at .% Co. The μ and R phases also extended in the same direction as at 1175 °C. The μ phase region was found to be a little more wide and the R phase region was found to be more narrow than in 1175 °C isothermal section. Another σ related phase, P phase, was found to exist between the μ and σ phases in the Co-Mn-Mo system at 1240 °C as a small elongated region parallel to the σ and μ phase regions.

The isothermal sections of the Co-Mn-Mo system (Fig. 4 and 5) show that compared with 1175 °C the extension of the σ phase at 1240 °C is more toward the Co-Mo system and this was interpreted, on the basis of the information available at that time, to be due to the σ phase in Co-Mo system being stable above 1250 °C. The accepted binary data of the Co-Mo system, however, shows that the σ phase is stable at ~1000 °C, with uncertainty in the temperature being very large, ± 100 °C. Since the σ phase exists in both Co-Mo and Mn-Mo systems in the temperature range of 1175° and 1240 °C, one should expect that at both these temperatures the σ phase should extend from one binary to the other in the Co-Mn-Mo system. Instead it shows more extension at the higher temperature 1240 °C than 1175 °C. This may possibly be due to sluggish reaction closer to the Co-Mo system and at 1175 °C the 72 h annealing possibly was not sufficient to produce proper phase equilibrium at the high Mo side of the ternary diagram. The Co-Mn-Mo system should be studied at the high Mo side with alloys annealed for a much longer period to establish proper phase equilibrium. The Co-Mo system also should be further studied to narrow down the lower temperature stability of the σ phase.

Reference

1960 Das: B.N. Das and P.A. Beck: "Relationship Between the Mn Phase and the Sigma Phase in the Mo-Mn-Co System," Trans. AIME, 1960, Vol. 218, pp 733-37 (Phase equilibria, #).

Co-Mn-Mo evaluation contributed by **K.P. Gupta,** The Indian Institute of Metals, Metal House, Plot 13/4, Block AQ, Sector V, Calcutta, India. Literature searched through 1993. Dr. Gupta is the Alloy Phase Diagram Program Co-Category Editor for ternary nickel alloys.